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Short Communication

Fracture behaviour of a polypropylene film

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A B S T R A C T

Ageing of polymers results from structural modifications at the molecular scale and kinetic modelling must be elaborated from analysis of the phenomenon at this scale. However, the change of mechanical properties results from modifications of structure at larger scale, especially the macromolecular scale (chain scission, crosslinking) and or at the macroscopic scale (skin-core structure linked to a superficial attack of the material).

The effect of photoageing on the behaviour of isotactic polypropylene films was studied on samples of weight average molar mass M_w = 270 kg mol^{-1}. The influence of photoageing on the fracture toughness was examined by using the Essential Work of Fracture (EWF) method. Complementary characterization was performed by FTIR, uniaxial tensile testing. In conclusion, EWF tests performed appear as an interesting method to characterize the influence of structural factors on the fracture properties of polypropylene.

1. Introduction

Polypropylene (PP) application is automotive parts, fibers for outdoor exposure, etc. have raised up an impressive amount of literature. It is now well known that this polymer is intrinsically reaction towards radical oxidation, even at ambient temperature, owing to the presence in the monomer unit, of easily abstractable tertiary CH bonds.

This process can be described, at least in a first approximation by the standard mechanistic scheme (Fig. 1).

Some kinetic properties of such "closed-loop" schemes, in which the reaction generates its own initiator (hydroperoxide), have been investigated in 1950 (Tobolsky et al.) and revisited in 2000 [1].

Schematically, the reaction displays an induction time of which the duration is inversely proportional to the initiation rate constant. In the case of photoageing, this latter is generally high, so that the induction period is short (for an unstabilized PP sample) or even inexistent, but the "closed-loop" character remains observable by some autoaccelerated shape of kinetic curves.

Indeed, the induction period can be considerably increased by pigments or UV absorbers (which decrease the photoinitiation rate by screen effect) or by radical scavengers such as hindered amines (HALS) [2].

Hydroperoxide photolysis leads primarily to highly reactive PO° and OH° radicals, which can rapidly abstract hydrogens to give P° radicals, but a very important characteristic of PO° radicals undergo a rearrangement easily by β scission leading to a chain scission. There is a large consensus on the fact that this latter is responsible for embrittlement. This latter occurs suddenly (when it is characterised by tensile testing), without significant changes of modulus or yield stress, at a very low conversion of the degradation process [3].

The sudden character of embrittlement indicates, no doubt, the existence of a critical structural state, but the exact nature of this critical state remains unclear: It could be a critical value of the molar mass, presumably linked to the entunglement density in the amorphous phase; a critical value of the tie chains (interconnecting crystalline lamellae) concentration, or a critical value of the crystallinity ratio X_c or, rather a critical value of the interlamellar distance l_a [4]. As a matter of fact, chain scission in the amorphous phase induces chemicrystallization, l_a e.g. induces an increase of X_c and a decrease of l_a, modifying thus eventually microdeformation mechanisms.

For the study of fracture properties in ductile samples, tensile testing call for certain criticism [5].

It seemed to us interesting to use Essential Work of Fracture (EWF), which is well known as a pertinent tool to investigate on fracture of ductile materials, especially in film geometry [6].

The method will be applied to the study of PP films photooxidation [3].

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Initiation	$\text{Polymer}(\text{POOH}) + h\nu \rightarrow P^*$
Propagation	$P^* + O_2 \rightarrow PO_2^*$
Propagation	$PO_2^* + PH \rightarrow POOH + P^*$
Termination	$P^* + P^*$, $P^* + PO_2^*$, $PO_2^* + PO_2^*$ } inactive products

Fig. 1. Photoageing closed-loop.

2. Experimental

2.1. Material

Extruded films of 100 μm thickness were made from a polypropylene (PP) homopolymer (3050MN1 from ATOFINA) stabilized by a mixture of Irganox 1010 and Irgafos 168 (0.5% by weight). The PP was selected because it can be considered as a model material according to its sensitivity to photoageing. The number and weight average molar masses, determined by size exclusion chromatography (SEC), were $M_n = 55$ kg mol^{-1} and $M_w = 270$ kg mol^{-1} respectively. The crystallinity ratio, determined by differential scanning calorimetry (DSC), was 65%.

2.2. Exposure

In order to achieve the irradiations, the PP films were exposed in reactors equipped with a fluorescent lamp ($300 < \lambda < 450$ nm; $\lambda_{max} = 365$ nm) at 70 °C in wooden frames 10×20 cm^2 (Fig. 2). These boundary conditions avoid edge effect, so that the film is considered infinite at the scale of heterogeneous oxidation phenomena.

3. Results and discussion

3.1. Chemical changes

The UV irradiation can be followed by monitored transform infrared spectroscopy (FTIR) based on the variation of the hydroxyl and carbonyl indexes. In order to record spectra, FTIR Bruker IFS 28 equipped with a computerized XY translational mapping system was used by steps of 20 μm. Figs. 3a and 3b present an illustrative example of the FTIR spectra of PP (a) before, (b) after photoageing. The absorbances of hydroxyl OH and carbonyl C=O bands were determined at 3400 cm^{-1} and 1720 cm^{-1} respectively. Note that

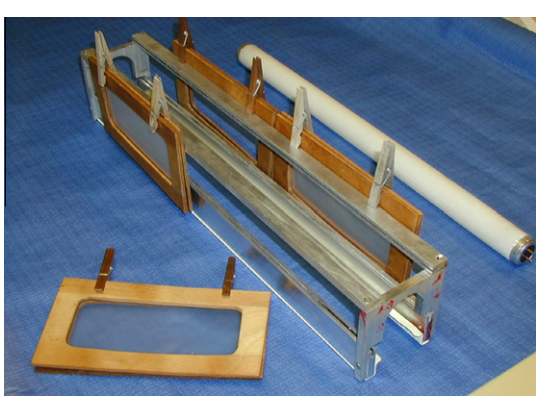

Fig. 2. Set-up for the photoageing of films.

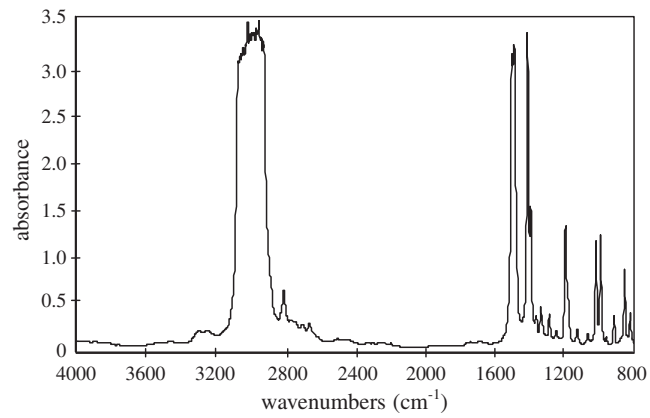

Fig. 3a. (a) FTIR spectra of unaged PP.

in the literature, the hydroxyl (OH) and the carbonyl (C=O) bands are considered as the most suitable indicators for photoageing in polypropylene. However, these indicators are significant only on the macroscopic scale. The absorbances of OH and C=O bands were converted into average concentrations using the Beer–Lambert law with molar absorptivity values of 70 l mol^{-1}cm^{-1} (OH) and 300 l mol^{-1}cm^{-1} (C=O) respectively:

$$c = \frac{A}{\alpha B} \tag{1}$$

where c is the concentration, A is the absorbance, α is the molar absorptivity and B is the sample thickness.

The kinetic curves of carbonyl and hydroxyl concentrations of the aged material are displayed in Fig. 4. Approximately an induction time of 370 h can be pointed out. The weight average molar mass M_w, determined by SEC, is plotted versus the exposure time in Fig. 4a. After an ageing time of about 330 h the decrease of M_w indicates that a chain scission process takes place during the induction period. Thus, the polymer embrittlement occurs at a very low conversion of the oxidation process. The weight average molar mass seems then to be a finer indicator of photoageing than OH and C=O concentrations.

3.2. Mechanical changes

After ageing, tension samples of 25 mm length and 4 mm width were cut out from the films using a MTS H2 stamp. Tensile tests were performed on an Instron machine under a nominal strain rate of 50 mm/min. It is found that the yield stress is not dependent on the exposure time. One can conclude that yield stress is not a convenient mean to describe the effect of photoageing. Furthermore, according to the literature, the ultimate stress cannot be considered as a representative endlife criterion for polymers [7,8]. On the other hand, the ultimate strain is generally considered as a suitable indicator of photoageing. As shown in Fig. 4b, the ultimate strain remains almost constant at a value of about 830% during the initial period of exposure and decreases abruptly after approximately 330 h. An induction time of 330 h, corresponding to this ductile–brittle transition can be thus highlighted. The sudden change from a ductile behaviour to a brittle behaviour can be explained by the presence of a critical structural state. At this ductile–brittle transition, the critical molar mass for embrittlement has a value of 195 kg mol^{-1}. The embrittlement of polymer, occuring at a very low conversion of the ageing, can be linked to tie molecules interconnecting lamellar which play a crucial role in fracture of yielding [9]. The oxidation in the amorphous phase

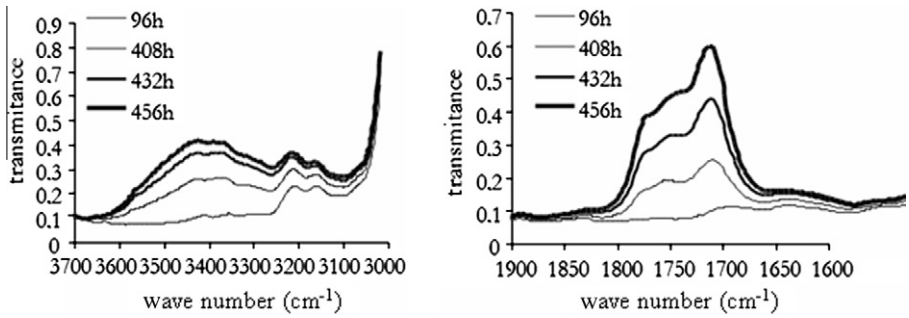

Fig. 3b. (b) 3000–3700 cm^{-1} and 1600–1900 cm^{-1} IR spectra evolution during PP oxidation at 70 °C.

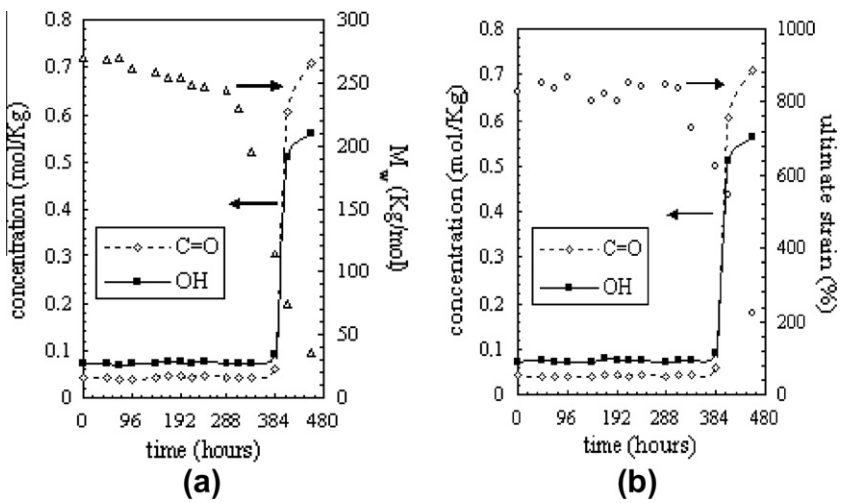

Fig. 4. Kinetic curves of C=O group at 1720 cm^{-1}, OH group at 3400 cm^{-1} and evolution during exposure of (a) average molar mass weight, (b) ultimate strain.

can lead to chain scission and then to rupture of ties chains producing a loss of ductility.

In order to investigate the ductile fracture behaviour of the PP film, it is very important to find appropriate experimental methodology. The fracture mechanics may be a suitable alternative to the traditional tensile tests achieved above. In this work, the fracture behaviour of the film was studied by two different approaches under mode I loading: the *J*-integral and the EWF theory.

The LEFM fails to provide proper fracture toughness values of highly ductile polymer films due to the large plastic zone created at the crack tip which is expressed by the energy dissipated during the blunting and the stable crack propagation precedes the fracture. In order to overcome this problem, an approach [10–12] for characterizing the polymer films based upon Broberg's suggestion [13] can be adopted: the EWF method.

In the EWF approach, the zone around the crack tip is divided into two regions: the inner fracture process zone (IFPZ) related to the actual fracture and the outer plastic deformation zone (OPDZ) related to shear yielding as shown in Fig. 5 for a double edge notch in tension (DENT) specimen.

The method consists of dividing the total energy for fracture W_f into two components: the specific essential work of fracture w_e and the specific non-essential work of fracture βw_p as illustrated in Fig. 6. To obtain these two components, the total work of fracture

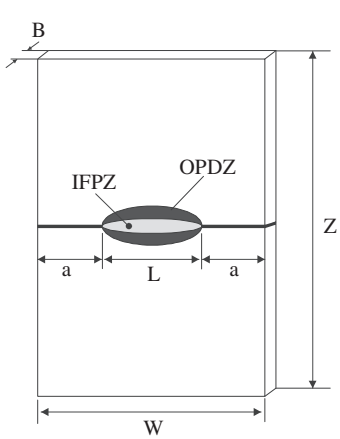

Fig. 5. DENT specimen geometry showing the OPDZ and IFPZ zones.

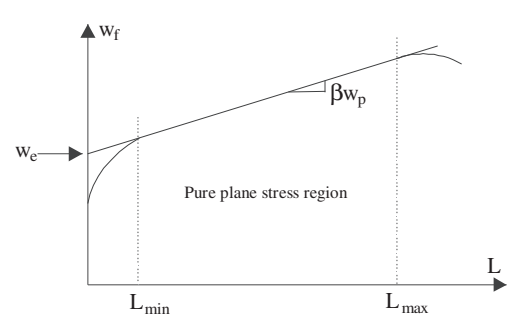

Fig. 6. Determination of EWF parameters.

W_f, recorded during the mechanical test and containing all the energy dissipated during the test, can be expressed by [10]:

$$W_f = \int P du = W_e + W_p \tag{2}$$

where P is the load and u is the displacement.

Assuming that W_e is proportional to the uncracked ligament area while W_p is linked to the volume of the plastic zone, it comes:

$$W_f = w_e LB + \beta w_p L^2 B \tag{3}$$

where B is the sample thickness, β is the shape factor of the plastic zone and $L = W - 2a$ is the uncracked ligament length (W being the sample width and $2a$ the initial total crack length). So that one has, per unit cross section:

$$w_f = \frac{W_f}{LB} = w_e + \beta w_p L \tag{4}$$

As schematically shown in Fig. 6, the work of fracture is plotted versus ligament length. Assuming a linear evolution, w_e is the ordinate at the origin and βw_p is the slope of the straight line. The component accounting for the essential work of fracture w_e and the plastic deformation term βw_p are expected to be independent on specimen geometry since the fracture process is in pure plane-stress configuration.

The films of polypropylene consist in sheets of 100 μm thin; rectangular samples of 25 mm width and 90 mm length were cut out from the sheets (clamped zones length equal to 55 mm, i.e. $Z = 35$ mm). DENT samples (Fig. 5) were precracked using a razor blade with ligament lengths L ranging from 6 to 16 mm [6]. Samples were tested in uniaxial tension using the Instron machine under a constant crosshead speed of 5 mm/min and at room temperature. The specimens were tested up to complete failure. Load–displacement curves examples are shown in Fig. 7 for various values of a/W ratio. These curves display a maximum which corresponds to the blunting due to complete ligament yielding (zone I in Fig. 7). Beyond this maximum, a slow decrease of the load corresponding to zone II, indicates slow stable crack growth in the yielded ligament, perpendicularly to the load direction.

The influence of photoageing on the specific essential work and non-essential work of fracture is given in Fig. 8. The EWF parameters show two zones of varying photoageing dependence. In the first zone ($0 \leqslant$ time $\leqslant 290$ h), they are more or less independent of photoageing, having an average value of about 58 kJ/m^2 for w_e

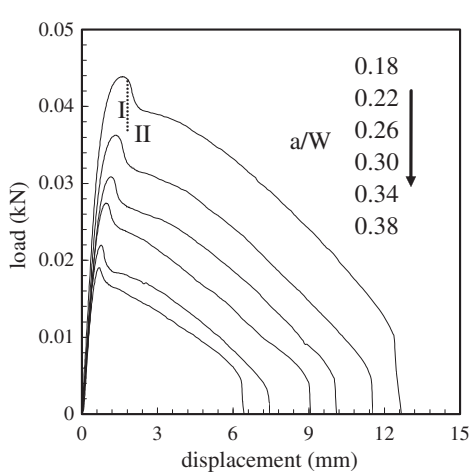

Fig. 7. Typical load–displacement curves as a function of a/W ratio.

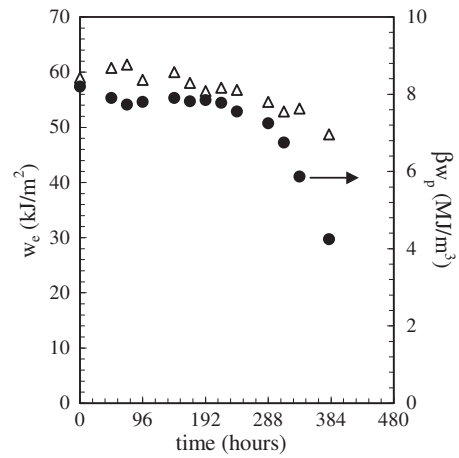

Fig. 8. Effect of ageing on the EWF parameters.

and 8 MJ/m^3 for βw_p. In the second zone (time > 290 h), w_e and βw_p decrease with the time of exposure and then with the embrittlement of polymer. The decrease of βw_p, caused by the scission of chains during the photodegradation, is more emphasized and the dependence of this parameter with photoageing implies that both the shape of the plastic zone β and the work dissipated in the plastic deformation zone w_p depend on photoageing. Furthermore, the plastic deformation term appears to be more sensitive to photoageing than the ultimate strain.

4. Conclusion

Polypropylene films were subjected to photoageing and its effect on physico-chemical and mechanical properties was investigated.

As ageing functions, polymer's chemical modifications were established. The structural modifications induced by the photoageing are well reflected in the changes of the molar mass, the carbonyl and hydroxyl groups.

The effect of ageing on the tensile and fracture toughness behaviour of the polymer was investigated. The ultimate strain can be considered as a good indicator of ageing. The EWF parameters were determined in the same configuration. Results indicated that the specific essential work of fracture w_e is not very sensitive to time of exposure while the plastic deformation term βw_p varies. It seems then that w_e cannot be considered as adequate variable being able to reflect the structural changes of this material caused by photoageing. The changes of the plastic properties, in term of βw_p and due to ageing, ultimate strain can be correlated with the photoageing and gives useful informations on the alteration. However, photoageing sensitivity of βw_p seems to be more remarkable than that of the ultimate strain.

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